



# Silver electrodeposition on the activated carbon air cathode for performance improvement in microbial fuel cells

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## H I G H L I G H T S

- Silver was electrodeposited on AC air cathode using a potentiostatic method.
- The maximum power density of the treated sample was 69% higher than the untreated.
- The ORR at the cathode took place through four-electron pathway.
- The total resistance of the electrodes was largely reduced.
- Ag deposition was not harmful to anode culture and improved cathode performance.

## A R T I C L E I N F O

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## A B S T R A C T

The present work was to study silver electrodeposition on the activated carbon (AC) air cathode for performance improvement in microbial fuel cells (MFCs). The treated cathodes were proved to be effective to enhance the performance of MFCs. The maximum power density of MFC with silver electrodeposition time of 50 s (Ag-50) cathode was  $1080 \pm 60 \text{ mW m}^{-2}$ , 69% higher than the bare AC air cathode. X-ray photoelectron spectroscopy (XPS) results showed that zero-valent, monovalent and divalent silver were present to transform mutually, which illustrated that the oxygen reduction reaction (ORR) at the cathode took place through four-electron pathway. From electrochemical impedance spectroscopy (EIS) analysis, the electrodeposition method made the total resistance of the electrodes largely reduced. Meanwhile the deposited silver had no toxic effects on anode culture but inhibited the biofilm growth of the cathodes. This kind of antimicrobial efficient cathode, prepared with a simple, fast and economical method, was of good benefit to the performance improvement of MFCs.

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## 1. Introduction

Facing today's energy resource depletion and environmental pollution, it is desirable to look for a kind of energy which can guarantee a sufficient supply for long-term and will not cause environmental problem. Nowadays, microbial fuel cells (MFCs) attract more and more attentions due to meeting the requirements. MFCs are devices which use electrochemical active microorganisms as the catalysts to oxidize organic and inorganic matter under ambient conditions and generate current [1]. Great progress has been made to improve the performance of MFCs in the last few years [2,3].

Compared to other oxidants, the most promising electron acceptor in the cathode for MFCs is oxygen due to the inexhaustible availability, high redox potential and the avoidance of energy intensive water aeration [4,5], so the air-cathode MFCs are becoming more popular. In such oxygen system, the cathode materials would largely affect the function of MFCs because of the poor kinetics of oxygen reduction in the medium [6]. Platinum is the most commonly used catalyst for oxygen reduction reaction (ORR), but its relatively high cost prohibits the practical application of large scale MFCs [7]. Therefore, it is very necessary to develop effective and low-cost catalysts to replace platinum. The electrochemical ORR on non-Pt catalysts are becoming highly sought for fuel cells applications [8]. Iron phthalocyanine [9], Co-naphthalocyanine (CoNPc) [10], carnation-like  $\text{MnO}_2$  [11] and so on, had aroused extensive research interest. Recently, a low-cost and effective activated carbon (AC) has become a hot spot. The cathode made with AC and polytetrafluoroethylene (PTFE) showed

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a comparable performance with a Pt cathode [12]. In addition, AC was a material for oxygen reduction that could produce a power density of  $750 \text{ mW m}^{-2}$  after a year, which showed that it had long-term performance [13]. So the AC air-cathode was applied extensively.

The price of silver is cheaper than platinum and as available electrocatalyst, silver had been applied in many reactions, which was active for chemical reduction of peroxide [12] and ORR [14], particularly in alkaline condition. Moreover, Ag-base catalysts had shown comparable performance to Pt at similar loadings, and the above two materials were able to promote the ORR via direct four-electron pathway [15].

In previous research, silver particles with various morphologies and surface chemical states were used as catalysts for ORR [16,17]. In addition, graphene or carbon black supported silver nanoparticle catalyst could enhance electrocatalytic activity towards ORR in alkaline medium [18,19]. Gong et al. used hydrothermal method to synthesize the carbon-supported nanometer silver/tungsten carbide hybrid (Ag–WC/C) as the cathodic electrocatalyst, which produced a comparable magnitude of power density to commercial Pt/C catalyst in MFC [20]. Graphite felt coated with silver nanoparticles as a cathode in MFC for microbial growth inhibition, led to a high current generation [21]. Electrodeposition is a simple, fast and economical method. Nowadays, electrodeposition technology has gotten great progress. Lv et al. prepared RuO<sub>2</sub>-decorated carbon felt anode in a way of cathodic electrodeposition, which resulted in the maximum power density increased by 17 times as compared to that obtained with the MFC with the bare anode [22].

However, there is little research about the performance and mechanism of treated ACs by electrodeposited silver in MFCs. In this study, silver was electrodeposited on AC cathode with different time (25 s, 50 s, 75 s) and the pretreated cathodes were evaluated in MFCs for their performance. Meanwhile, tests were used to investigate the catalytic mechanism of silver electrodeposited on AC.

## 2. Materials and methods

### 2.1. Electrode materials and chemicals

Air cathodes consisted of a stainless steel mesh with a gas diffusion layer (GDL) and a catalyst layer (CL). And all the air cathodes were made by rolling-press method [23]. The GDL was prepared by carbon black and PTFE with a mass ratio of 3:7 and then heated at  $340^\circ\text{C}$  for 20 min, while CL was made of AC ( $2100 \text{ m}^2 \text{ g}^{-1}$ , Yihuan Carbon Co. Ltd., Fujian, China) and PTFE with a mass ratio of 6:1 [24]. The amount of AC used in each CL was about 0.3 g. The prepared cathodes were modified by electrodeposition with potentiostatic plating technique. The electrodeposition was carried out using a Corrtest CS120 model electrochemical workstation (Wuhan, China) in a conventional three-electrode cell with Ag/AgCl (0.195 V versus standard hydrogen electrode) as reference electrode and platinum sheet as counter electrode. Silver was electrodeposited on the surface of AC with a potentiostatic polarization voltage of  $-0.8 \text{ V}$  [25]. The electrolyte was AgNO<sub>3</sub> (2.2 mM, pH = 11) solution. Silver was electrodeposited successively with different time. The deposition time was 25 s, 50 s and 75 s, namely Ag-25, Ag-50 and Ag-75. For each deposition time, three cathodes were made to determine the reproducibility of data. Thus, 12 cathode samples were prepared. The remaining silver nitrate was recycled. The anode was carbon felt which was immersed in acetone for 12 h and then was washed with distilled water for 3 or 4 times before putting it into the MFC.

### 2.2. MFC construction and operation

The single-chamber MFCs were constructed with an inner cylindrical chamber 3 cm in diameter and an electrode spacing of 4 cm [26]. The inner volume was 28 mL. Both electrodes had a projected area of  $7 \text{ cm}^2$ . Titanium wire had highly anti-corrosion and good conductivity, so it was used to connect the anode and cathode with the whole circuit to transfer the electrons. The external resistance was  $1000 \Omega$ . Domestic waste water was used as the inoculum. In the first 3–4 cycles (one cycle 1–2 days) of cell culture, the nutrient solution consisted of waste water and 50 mM phosphoric acid buffer solution (PBS, pH = 7) with sodium acetate ( $1 \text{ g L}^{-1}$ ) as the substrate. The PBS contained NH<sub>4</sub>Cl ( $0.31 \text{ g L}^{-1}$ ), KCl ( $0.13 \text{ g L}^{-1}$ ), NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O ( $3.321 \text{ g L}^{-1}$ ), Na<sub>2</sub>HPO<sub>4</sub> ( $4.090 \text{ g L}^{-1}$ ), trace mineral ( $12.5 \text{ mL L}^{-1}$ ), and vitamin ( $5 \text{ mL L}^{-1}$ ) solution [27]. All the reactors were controlled at  $30^\circ\text{C}$  and the voltages of MFCs were recorded every minute by data acquisition card (Morpheus Electronic Co. Ltd, Beijing, China).

### 2.3. Electrochemical and material analysis

Polarization curves and power density curves were obtained by varying the external resistance from  $9000 \Omega$  to  $50 \Omega$ . Each resistor was tested for fixed time (about 10 min) to ensure a stable voltage. Cathode and anode potentials during polarization were measured using Ag/AgCl as a reference electrode. Linear sweep voltammetry (LSV) of all the cathodes were tested by a potentiostat (Wuhan, China). LSV was conducted from OCP to  $-0.3 \text{ V}$  with a scan rate of  $0.1 \text{ mV s}^{-1}$ . Ag/AgCl (saturated KCl) was used as reference electrode and platinum sheet ( $1 \text{ cm}^2$ ) was used as counter electrode. The voltages in the text were measured with Ag/AgCl as reference voltage. These two electrodes were both fixed with a  $0.5 \text{ cm}$  spacing from the working electrode. Before the tests, the cathodes should be immersed in 50 mM PBS for about 24 h.

Electrochemical impedance spectroscopy (EIS) of all the cathodes was performed over a frequency range of  $100 \text{ kHz}$ – $10 \text{ mHz}$  at open circuit potential [28] using a potentiostat (CHI600E, ChenHua Instruments Co., Ltd., Shanghai, China). Tests of treated or untreated AC cathodes were kept under the same conditions, such as using the same electrolyte and fixed reference electrode.

X-ray photoelectron spectroscopy (XPS) was employed to obtain information about the valence of deposited silver species on the surface of AC. The measurements were carried out using an XPS spectrometer (K-Aepna, Thermo Fisher Scientific Inc., USA). Survey scans of Ag3d, C1s, and O1s core-level spectra were taken for the most effective silver/carbon sample (Ag-50). The deconvolution of the main Ag3d peaks was performed by applying Casa XPS software and the positions were determined according to reports from the literature and empirically derived values. In addition, the peaks for silver element were calibrated with reference to C1s ( $284.6 \text{ eV}$ ).

Scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer was applied for analyzing the morphology of the modified and bare AC surface using S–3500N made by Hitachi. The structures magnified 40,000 times were respectively observed and compared.

Inductively coupled plasma optical emission spectrometry (ICP-OES) was employed to detect whether silver element existed in the solution and the microorganisms of the anode and cathode using IRIS Intrepid II XSP made by Thermo Elemental company in the USA. The measurement was carried out using an ICP-OES spectrometer. Ag-75 cathode was used as the test sample because it had the highest silver content. Before testing, a certain amount of the solution taken from the cell was filtered through a  $0.2 \mu\text{m}$  membrane filter. The filtered solution was used for test. A small amount of microorganisms was scraped from the surface of the electrodes

and then taken into the distilled water respectively. Add several drops of dilute nitric acid in aqueous solution and digest it at 100 °C until all the microorganisms was transformed. The digested solution was then filtered through the membrane filter for test.

### 3. Results and discussion results

#### 3.1. Performance of different air cathodes

The voltages of the external resistances were up to about  $490 \pm 10$  mV after cell operation for two weeks. Polarization curves and power density curves were measured after one month in order to obtain a mature anodic biofilm.

The results of power densities are provided in Fig. 1a, which show that the electrodeposition of silver on AC air cathode has significant effects on the performance of MFCs. The MFC with bare AC cathode had the maximum power density of  $639 \pm 60$  mW m<sup>-2</sup>. With the deposition time increasing from 25 s to 75 s, the maximum power density showed a downward trend after first rising, but little difference on the whole. The MFC with Ag-50 cathode produced the maximum power density of  $1080 \pm 60$  mW m<sup>-2</sup>, with a value 69% higher than that of untreated AC. While MFC with Ag-25 and Ag-75 cathodes had the power density of  $927 \pm 60$  mW m<sup>-2</sup> and  $1046 \pm 60$  mW m<sup>-2</sup> respectively. The cathode and anode polarization curves (Fig. 1b) showed that for all four MFCs, the anode potentials were similar, but the performances of the cathodes were much different with the increasing

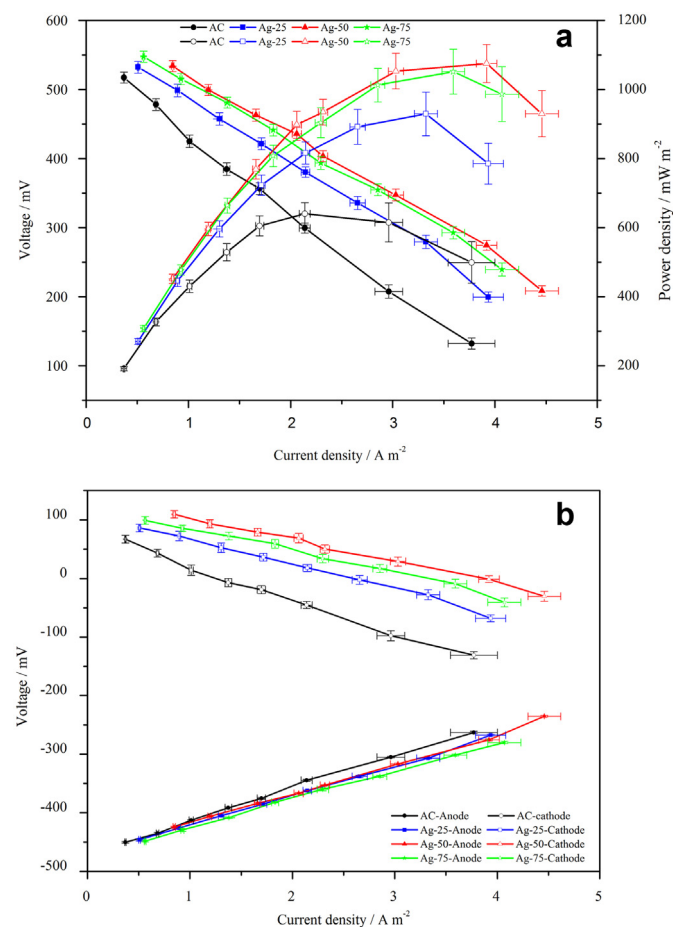
order: Ag-50 cathode > Ag-75 cathode > Ag-25 cathode > AC cathode. Moreover, from the point of view of each cathode voltage trend, the cathodic polarization of AC was much more serious than that of the rest three cathodes. The results indicated that the increase of cathode performance was responsible for the improvement of the power output, while anode performance had little influence on it.

The maximum power density of the air cathode produced by electrodeposition method was compared to that prepared by Pt catalyst [12]. Moreover, the cost of producing the electrodes was greatly reduced, so silver electrodeposition on AC could be an effective and low-cost cathodic catalyst alternative to Pt for ORR. Besides, MFC with the synthesis of Ag-WC/C as a cathode using hydrothermal method produced a maximum volumetric power density of  $20.62$  W m<sup>-3</sup> ( $824.8$  mW m<sup>-2</sup>) [20], which was lower than that of direct silver electrodeposition method, and the electrodeposition method was much easier and quicker. In Liu's research, manganese oxides electrodeposited on carbon paper was used as the cathode, MFC with which produced much lower power density ( $772.8$  mW m<sup>-3</sup> or  $386.4$  mW m<sup>-2</sup>) [4]. This was possibly because that the performance of carbon paper was much poorer than that of AC.

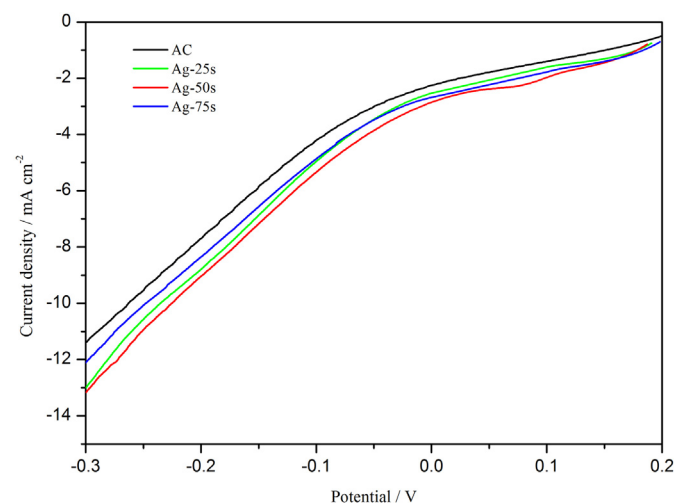
#### 3.2. Electrochemical characterization

Fig. 2 shows the results of the LSV for the AC air-cathode with different electrodeposition time of silver. The most critical performance of these cathodes was dropped in the potential range of 0.1 to -0.1 V. LSV curves showed that when the potential was greater than -0.06 V, the current density of Ag-25 cathode was higher than that of Ag-75 cathode, but when the potential was less than -0.06 V, the result was opposite. At the potential of 0 V, the current density of Ag-50 cathode was  $2.85$  mA cm<sup>-2</sup>, which was 27% higher than that of the bare AC air electrode ( $2.25$  mA cm<sup>-2</sup>). All the three AC air cathodes deposited with silver had a significantly higher current density than the bare AC air-cathode, indicating that silver was beneficial for ORR on the electrode. The currents obtained in real abiotic LSV curves were comparable with those obtained in real MFCs, which indicated that the biological contamination on activated carbon cathodes had little effect on current output [24].

The improved ORR performance could also be verified by EIS analysis. An equivalent circuit for porous electrode was used as



**Fig. 1.** Performance of MFCs equipped with bare AC air cathode and Ag-25, Ag-50, Ag-75 cathodes: (a) power density and cell voltage curves and (b) cathode and anode polarization curves.



**Fig. 2.** LSVs of the AC air cathode and Ag-25, Ag-50, Ag-75.

previously reported by Wang et al. [24] The equivalent circuit was consisted of an external ohmic resistance mainly due to the electrolyte between the counter electrode and the air-cathode surface ( $R_0$ ), a diffusion resistance which was an electronic resistance of the current collector and contact resistances ( $R_d$ ), a charge transfer resistance ( $R_{ct}$ ), double layer capacitances ( $C_{dl}$ ), pore adsorption capacitance ( $C_{ad}$ ) distributed between the ohmic and Faradic processes, and a Warburg impedance ( $W$ ). The status of each cathode was considered the same and comparable (zero current output) because the EIS tests of all cathodes were carried at their OCPs.

Fig. 3 and Table 1 indicate that the total resistances of all the air-cathodes after silver deposition show a clear decrease, which has positive effects on the increase of the power density. But EIS results were not completely consistent with the maximum power densities. Although the total resistance of Ag-75 was a little bigger than that of Ag-25, Ag-75 showed higher power density, which indicated that the cathodic resistance was not the only factor affecting the performance of MFC. There should be other factors such as the impact of the quantity of deposited silver on AC, the catalytic activity of silver and so on. Among all the resistances, the charge transfer resistance was dominant. Each modified air cathode decreased  $R_{ct}$  compared with the bare AC air cathode, of which Ag-50 cathode showed the most significant effect. It decreased the  $R_{ct}$  by 33% from 13.41  $\Omega$  (AC cathode) to 8.98  $\Omega$  (Ag-50 cathode). This phenomenon demonstrated that the treatment of silver electro-deposition could accelerate the charge transfer processes. In addition, the ohmic resistances of different cathodes were almost the same, which might be the consequence of the same PBS electrolyte used in the experiments.  $R_d$  of air-cathodes exhibited the decreasing trend after treatment, indicating that the treatment was able to enhance the surface conductivity. These air cathodes could be regarded as capacitances in the equivalent circuit. The treatment increased the double layer capacitances ( $C_{dl}$ ) as well as the adsorption capacitances ( $C_{ad}$ ). With the increase of silver deposition time,  $W$  was gradually reduced, which revealed that silver deposition had a positive effect on diffusion condition.

The total resistance of the prepared electrodes was compared to that of the electrode with Pt/C catalyst (16.4  $\Omega$ ) and the smallest resistance was almost the same as that of MnO<sub>2</sub>-graphene hybrid catalyst (12.4  $\Omega$ ), which was reported by Wen et al. [29]. Moreover,  $R_{ct}$  of the prepared cathodes was much smaller than that of graphite felt cathodes coated with silver nanoparticles ( $30.80 \pm 0.2$   $\Omega$ ) [21].

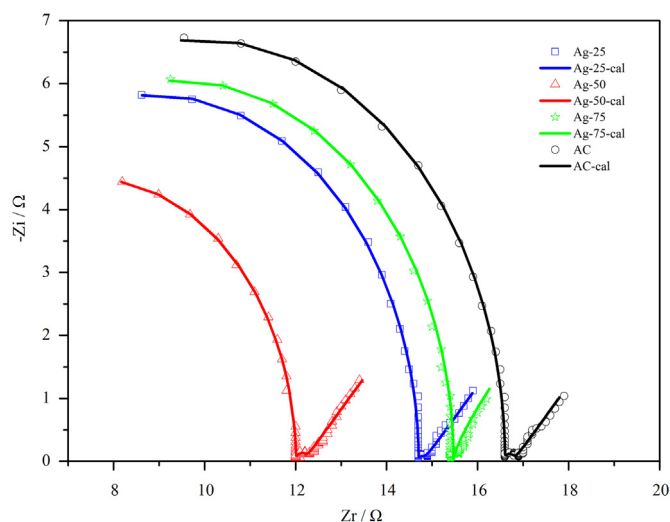


Fig. 3. Nyquist plots of EIS by bare AC air cathode and Ag-25, Ag-50, Ag-75 cathodes. Lines marked as 'Cal' were fitting data from the equivalent circuit.

Table 1

Fitting results of different cathodes based on the equivalent circuit.

	AC	Ag-25	Ag-50	Ag-75
$R_0$ ( $\Omega$ )	3.195	3.059	3.02	3.367
$C_{dl}$ ( $10^{-7}\Omega^{-1} s^n cm^{-2}$ )	1.53	1.73	1.85	1.64
$R_d$ ( $\Omega$ )	0.1877	0.1126	0.1739	0.000815
$C_{ad}$ ( $\Omega^{-1} s^n cm^{-2}$ )	0.01058	0.01862	0.01241	0.1381
$R_{ct}$ ( $\Omega$ )	13.41	11.65	8.979	12.1
$W$ ( $\Omega s^{-1/2}$ )	1.565	1.335	0.8397	0.4916

This demonstrated that the prepared cathodes had a greater charge transfer rate and could produce larger amount of exchange current.

### 3.3. Oxygen reduction reaction mechanism analysis

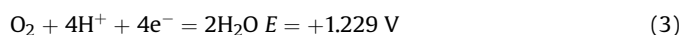
The surface composition and elemental analysis for AC and Ag-50 cathodes were characterized by XPS technique. Fig. 4a shows that AC cathode is composed of elements C1s, O1s and F1s. Elements of C1s, O1s, F1s and Ag3d were revealed from Ag-50 cathode (Fig. 4b). The existence of F element was due to the use of PTFE as a binder in the preparation of catalyst layer. Fig. 4c shows the high-resolution Ag3d<sub>5/2</sub> spectra resolved into three individual component peaks: peak 1 at 367.3 eV due to the presence of the AgO species; peak 2 at 367.8 eV and peak 3 at 368.3 eV corresponding to the presence of Ag<sub>2</sub>O and zero-valence silver atoms, respectively [30].

XPS result showed the presence of monovalent and divalent silver, so we hypothesized that the reaction of silver was as follows:

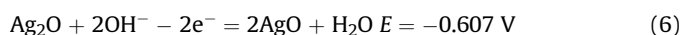
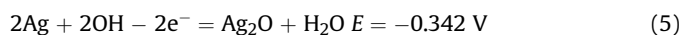


The air-cathode was in close contact with the air. The pores formed by PTFE and carbon particles of both CL and GDL were considered as the channels for gaseous transport, so the surface silver could be in good contact with the subsurface oxygen and surface oxygen. The certain volumes of oxygen were absorbed by a technical silver catalyst under certain pressure and temperature by physical adsorption and chemisorptions methods [31]. It was indicated that Ag<sub>2</sub>O was a reaction intermediate and AgO was a final product.

Electrochemical activity of the air cathode modified by deposited silver was studied in the reaction of molecular oxygen reduction. There were two types of oxygen reduction products, namely H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O [32], through two-electron and four-electron transfer, respectively, which corresponded to the following formulas of standard potential:

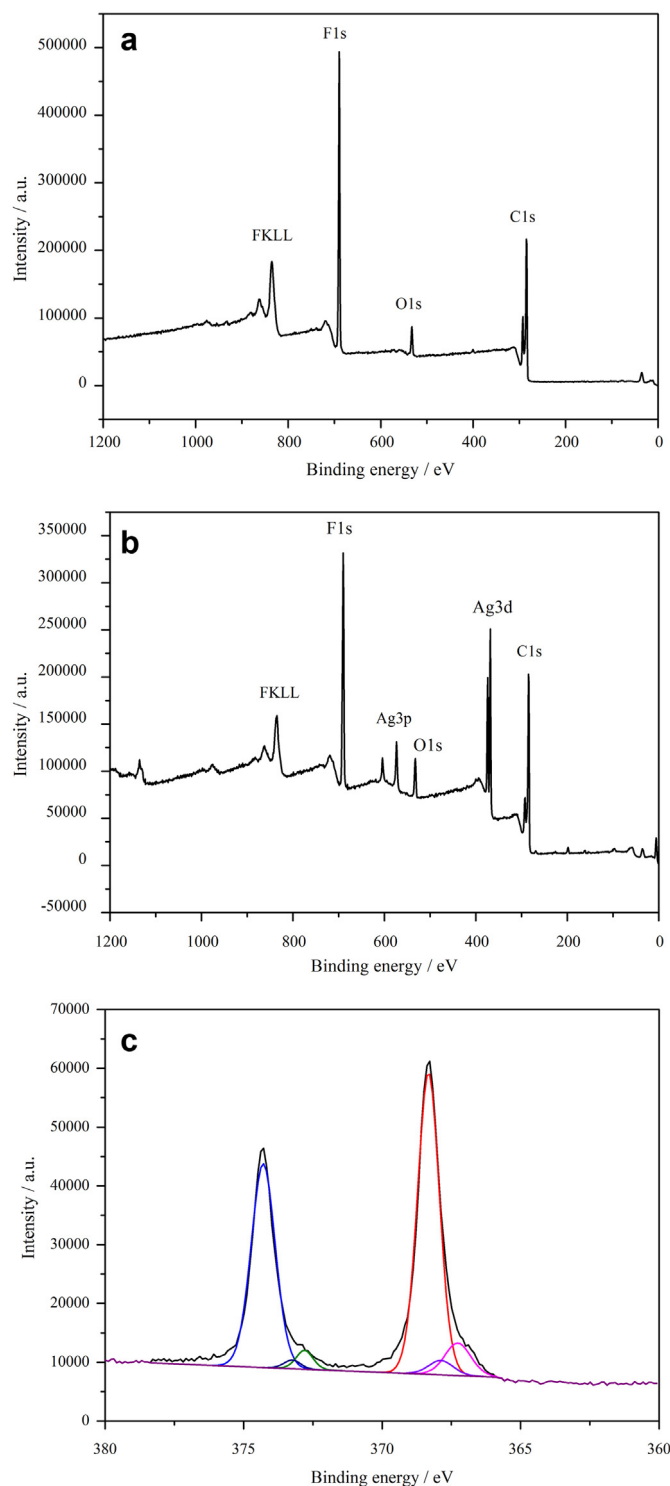


And the formulas of standard potential about oxidation of silver were as follows:



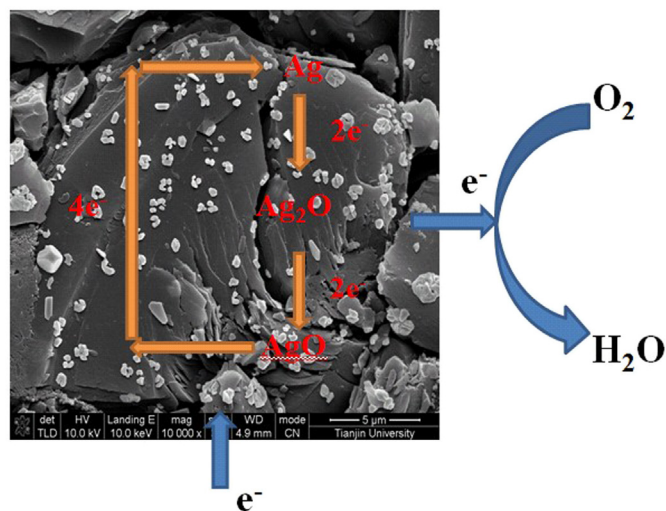
The standard potential indicated that two-electron transfer could not oxidize silver from zero valence to divalence. Only four-electron transfer could meet the requirements. So the ORR at the cathode took place through four-electron pathway. And during the operation





**Fig. 4.** The XPS spectrum measured on the bare AC air cathode (a) and Ag-50 cathode (b). High resolution XPS Ag-3d peaks obtained from Ag-50 cathode (c).

of MFCs, it was easy for AgO to accept electrons from the cathode and eventually be reduced. The charge transfer schematic was shown in Fig. 5. The monovalent and bivalent silver could coexist in the mutual transformation. In previous researches, silver-gas diffusion electrodes were prepared by direct deposition of the catalyst onto a carbon paper and the ORR occurred via a four-electron pathway on the Ag electrodeposited [33]. In addition, silver monolayer islands deposited on gold substrate also showed the original ability of four-



**Fig. 5.** The schematic of charge transfer process.

electron reduction [34]. The above obtained result was consistent with the previous research results, which demonstrated that silver exhibited high catalytic activity. Mutual transformation between different valence state of silver was helpful to accelerate the rate of electron transfer, which was an important reason for the excellent performance of MFCs with modified cathodes.

### 3.4. The morphology of different cathodes

As seen from the results of SEM (Fig. 6), different silver deposition time had little effect on the morphology of different cathodes. It was clear that with the increase of deposition time from 25 s to 50 s, the size of silver particles also increased (increasing from 470 nm to 580 nm), randomly distributing on the surface of the activated carbon. This could increase the conductivity of the electrodes. While with the continued increase of deposition time, the silver particles became larger (740 nm). It was reported that silver with a smaller size had higher mass activity with the same load on carbon paper, while with the same particle size, lower silver loading samples had higher mass activity [33]. The silver particles of Ag-25 and Ag-50 cathodes were much smaller than that of Ag-75 cathode, so they both exhibited relatively higher activity, while Ag-75 cathode behaved lower activity due to the larger size. Ag-25 cathode might have higher activity than Ag-50 cathode with lower loadings, but it had a slightly larger resistance than Ag-50 cathode due to the conductivity possibly. The results were almost consistent with the EIS analysis. As a result, the increase or reduction in the amount of the electrodeposited silver was not necessarily beneficial to improve the performance of the electrodes. Silver deposition quantity was not a decisive factor of MFC performance.

### 3.5. Effects of silver on microorganisms

The ICP-OES was employed to determine whether there was silver element in the microorganisms of the electrodes and solution. The results are summarized in Table 2. As was indicated, there were 0.0070 ppm, 0.0025 ppm and 0.0007 ppm of silver in the anode microorganisms, cathode microorganisms and culture solution respectively. The stddev was very small, namely 0.0034, 0.0036, 0.0058. The content was too low to ignore the existence of silver. In addition, The XPS showed that the silver was present in the form of zero-valence silver, Ag<sub>2</sub>O and AgO, so that no silver ions were free from the cathode surface. The above indicated that no

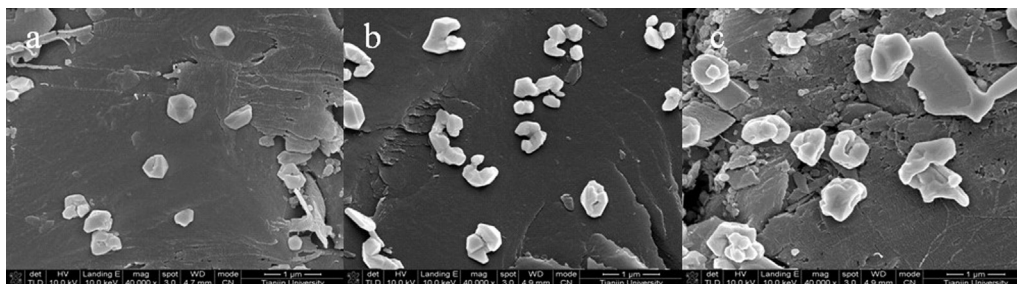


Fig. 6. SEM images of the surface of Ag-25 cathode (a), Ag-50 cathode (b), Ag-75 cathode (c) at the magnification of 40,000.

Table 2

The content of silver in the solution and the microorganisms of the anode and cathode.

	Elem	Avg	Units	Stddev
Sample-anode	Ag3280	0.0070	ppm	0.0034
Sample-cathode	Ag3280	0.0025	ppm	0.0036
Sample-solution	Ag3280	0.0007	ppm	0.0058

silver substance diffused from the cathode, which was firmly deposited on the surface of the activated carbon. Thus we could conclude that silver electrodeposition on the cathode had no harmful effect on anode microorganisms.

After MFCs cultured for a period, microorganisms always grew on the surface of the anode. Meanwhile, a biofilm was also formed on the cathode, which inhibited abiotic ORR on the cathode to decrease the performance, and the power density would increase when the biofilm was removed [35,36]. Further to say, the biofilm development induced the degradation of the AC catalyst performance and finally impaired power generation due to clogging of the AC micropores [13]. Therefore, the performance of the cathodes would reduce after a period of operation due to the influence of surface microorganisms. However, the silver decorated AC could inhibit the biofilm growth of the cathodes just because the electrodeposited silver on AC had the antimicrobial property and the bactericidal effect [37]. Silver electrodeposition on AC made microorganisms difficult to be attached to the cathode surface, which hardly reduced the catalytic properties of AC. This kind of cathode could be said to be an antimicrobial efficient electrode, which showed great advantage compared to other modified electrodes. Moreover, silver electrodeposition had no toxic effects on the anode because no free silver ions reached the anode. Therefore, the performance of all MFCs would be improved.

#### 4. Conclusion

AC air cathode with electrodeposited silver was effectively used in single-chamber MFCs to generate current. The ORR catalyzed by the modified cathodes proceeded a four-electron pathway and the electrodeposition method made the total resistance of the electrodes largely reduced. In addition, silver electrodeposition on the AC air cathode had antimicrobial property to cathode microorganisms; however there was no toxic effect on anode culture. The method of preparing the cathodes is simple, fast, economical and efficient, which will have some significance on the improvement of cathode performance and further research on MFCs.

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